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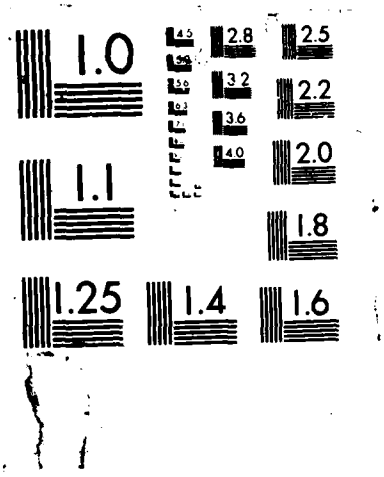
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ELECTRONIC STRUCTURE OF α-QUARTZ AND THE INFLUENCE OF SOME LOCAL DISORDER: A TIGHT BINDING STUDY

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ABSTRACT

A study of the electronic structure of α-quartz, the influence of short range departure from the α-quartz geometry, and the correlations between charge transfer from Si to Oxygen with variations in Si-O-Si bond angle is presented. For the first time, a framework is presented and utilized to shed light on the nature and origin of the several recently observed Si(2p) levels in XPS studies of bulk a-SiO_2 as well as the interfacial region near the Si/SiO_2 interface.

In this paper we report the results of (i) a tight-binding study of the electronic structure of α-quartz, including second-nearest neighbors, (ii) some changes in this electronic structure caused by short range departures from the α-quartz geometry, and (iii) an analysis of the Si(2p) core level chemical shifts in a-SiO_2 and near the Si/SiO_2 interface, from which some inferences regarding the chemical and structural nature of this interface are drawn for the first time. The calculations are motivated by ongoing ESCA studies[1,2] of the Si/SiO_2 system in which continuous monitoring of the valence and core levels, as a function of the oxide thickness, have revealed an interfacial region, about 7 Angstroms thick, and of chemical composition SiO_x, $x < 2$. The flexibility of the tight-binding method is exploited to simulate the influence of variations in the Si-O-Si as well as the O-Si-O angles on the band structure, density of states, and charge distribution. Calculated changes in the charge transfer from Si to Oxygen are, for the first time, correlated with the observed chemical shifts[2] of the Si(2p) core levels in bulk a-SiO_2 as well as in the interfacial SiO_x layer.

The tight-binding integrals in our study of α-quartz are treated as parameters and determined by fitting to the recent pseudopotential based band structure calculation reported[3] by Chelikowsky and Schluter. An extended summary of the theoretical and experimental work on SiO_2 is to be found in that paper. The tight-binding basis consists of the four sp^3 hybrids on each of the three Silicon atoms and the three p

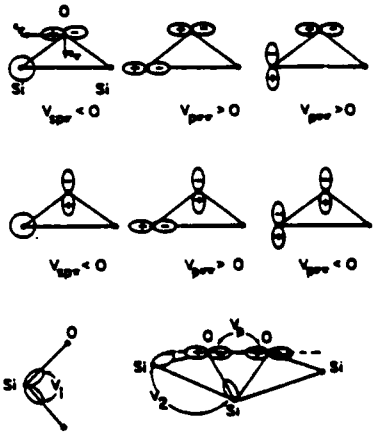

Fig. 1 Shows the various atomic matrix elements used in the text.

orbitals centered on each of the six Oxygen atoms in the hexagonal primitive cell of α-quartz. We neglect the Oxygen 2s state. The lowest eighteen of the thirty bands so obtained correspond to the valence bands. The system is viewed as alternating Si-O-Si and O-Si-O triads. Defining the unit vectors ε_σ and $\varepsilon_{\pi 1}$ as shown in Fig. 1, and $\varepsilon_{\pi 2}$ normal to the Si-O-Si plane, we note that the $p_{\pi 2}$ Oxygen orbital interacts weakly with the Si orbitals. The topmost valence bands are largely derived from these orbitals and have consequently been referred to as "non-bonding." The matrix elements, in terms of atomic orbitals, are defined as in Fig. 1. In Table I we provide two sets of tight-binding parameters. The first set gives a good fit to the non-bonding valence bands and the low-lying conduction bands of the pseudopotential calculations. The corresponding band structure and density of states (DOS) are shown in Fig. 2 and Fig. 3 respectively. The second set yields a good fit to all the valence bands at some expense to the conduction bands and to the indirect gap. The valence band density of states for this case is shown in Fig. 4. A Gaussian width of .5 eV was used in the DOS calculations. The non-bonding bands are found to have largely Oxygen p character with only a little Si s and p mixing, while the lower bonding valence bands have mixed Si-s, Si-p, and Oxygen-p character. A more detailed description will be published elsewhere. In brief, the diagonal energies control the basic separation between conduction and valence bands, $V_{sp\sigma}$ and $V_{pp\sigma}$ control the widths of the upper conduction and lower valence bands, and $V_{sp\pi}$ is a "fine tune" for the gap at the Γ point due to the pure s-character of the conduction band and p-character of the valence band at that point. The other nearest neighbor parameters yield only secondary effects. As for second neighbor parameters, we find that the band structure is not very sensitive to V_2 but that V_p is crucial in determining the width of the non-bonding bands. It is of interest to note that the indirect gap arises from a second order effect involving the O-Si interaction, $V_{pp\pi}$. It was only when this parameter was made large, and with $V_p \neq 0$, that an indirect gap was obtained. The price to pay was a lowering of the lower-lying valence bands.

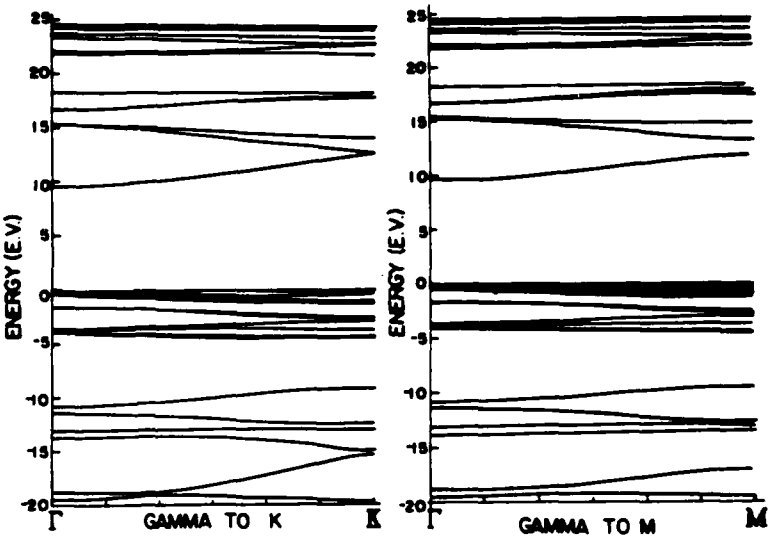

Fig. 2 Energy bands corresponding to the parameters (set 1) of Table I.

The valence band DOS weighted by the appropriate[5] s and p photoelectric cross-sections at 1487 eV is shown in Fig. 5 (curve a) for comparison with XPS spectra for α-quartz[4] (curve b) and a-SiO_2[2] (curve c). The relative intensities of the bonding and non-bonding valence band regions can be brought into better agreement with experiment by increasing the ratio of s to p photoelectric cross-sections. The larger width of the bonding valence bands and the sharp peak at the non-bonding valence band edge are a consequence of fitting to the pseudopotential calculations which also show the same discrepancy. The calculated charge transfer from Si to Oxygen for α-quartz is found to be

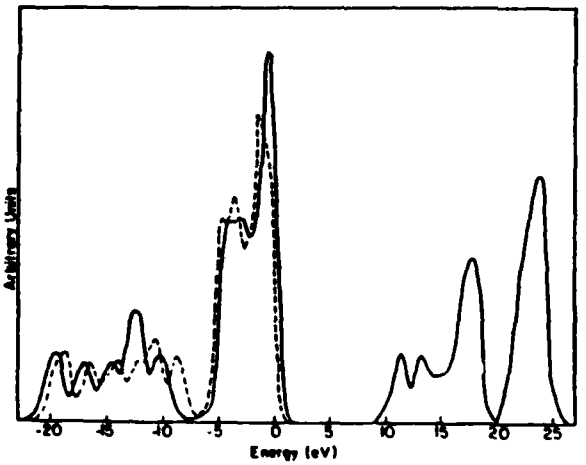

Fig. 3 Density of states corresponding to the parameters (set 1) of Table I.

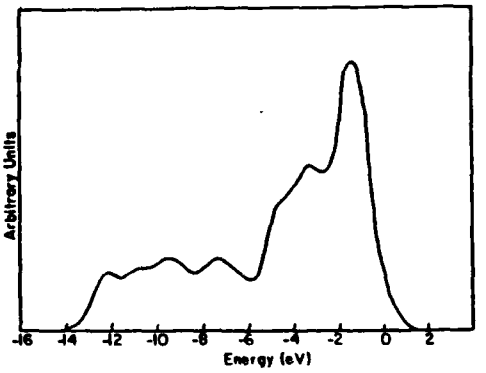

Fig. 4 Valence band density of states corresponding to the parameters (set 2) of Table I.

about 1.17 electron.

The basic mechanisms of our model having been exposed, we wish to exploit the built-in flexibility of such a scheme to examine the effect of various deformations.

(a) Si-O-Si Bond Angle Changes

The changes in the DOS as a function of the Si-O-Si bond angle were examined. The DOS for a Si-O-Si bond angle of 130° is shown by the dashed line of Fig. 3. We note the appearance of states in the "gap" between the two sets of valence bands, as well as the displacement of the non-bonding valence band edge to lower energy, thereby increasing the fundamental gap. The opposite effect is found when the angle is made larger than the α-quartz value of 144°.

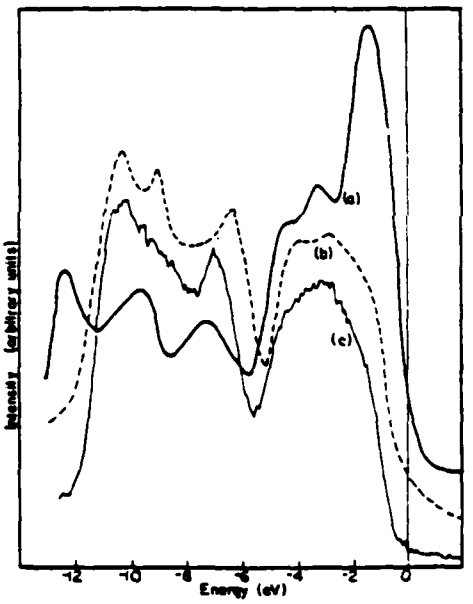

Fig. 5 Photoelectric cross-section weighted density of states as described in text.

(b) O-Si-O Tetrahedral Angle Changes

The major changes in the electronic structure due to variations in the tetrahedral angle arise from changes in the O-O interactions. This fact is illustrated in Fig. 6 where we have compared the following three curves: the non-bonding valence band DOS corresponding to set 1 of Table I (Fig. 6a), the DOS for a smaller tetrahedral angle when only the changes in the nearest neighbor parameters are included (Fig. 6b), and finally (Fig. 6c) the DOS when changes in all the parameters are kept. It is seen that the smaller tetrahedral angle, which corresponds to a smaller O-O distance and therefore a larger interaction matrix element, V_p, gives rise to a broadening of the non-bonding valence band. The opposite effect is observed for larger tetrahedral angles.

We now turn to an analysis which, for the first time, correlates the valence band charge densities, as a function of the Si-O-Si bond angle, to the several different Si(2p) core level chemical shifts[2] observed in a-SiO_2 as well as in the interfacial region. This analysis has enabled us to suggest the possible distribution of the Si-O-Si bond angles and the ring sizes that may be associated with them. In addition, within this conceptual framework we are able to shed light on the presence of possible suboxides, ranging from Si_2O_3 to Si_2O, in the interfacial region.

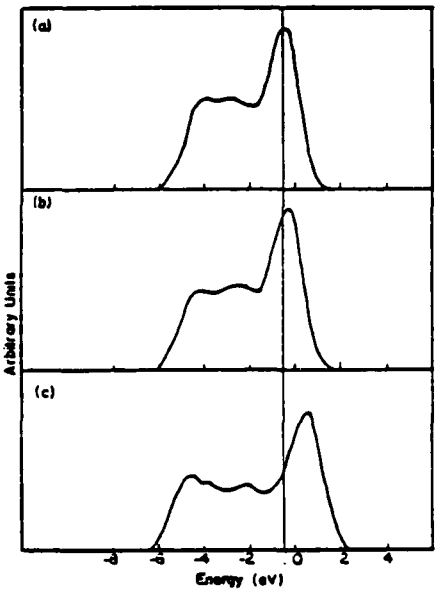

Fig. 6 Shows the influence of the change in the O-Si-O tetrahedral angle. Valence band edge of α-quartz (curve a) marks the energy zero.

Recent XPS measurements[2] have revealed the presence of several Si(2p) core levels in a-SiO_2, as well as in the neighborhood of the interface (see Table II). The presence of these peaks has been taken to indicate differing local structural and chemical environments, in both cases.[2] Considerable evidence for fluctuations in the Si-O-Si bond angle (θ) in glasses has been accummulated over the years.[6] This suggests the possibility that the different chemical shifts observed reflect the influence of loss of charge from Si to Oxygen for different most likely values of the Si-O-Si bond angle, possibly corresponding to a distribution of ring sizes ranging from 4 to 8. We therefore calculated the Si to Oxygen charge transfer for various values of θ of which θ = 120° and θ = 144° are known[6] to correspond to 4 and 6 membered rings. From the observed difference of Si(2p) levels in Si element and SiO_2, and the calculated value of 2.34 for the total charge loss per Silicon for α-quartz, we obtain an estimate of the chemical shift per unit charge, within the accepted linear approximation. Employing this value, we calculate the Si(2p) core level shift as a function of θ. Comparison with experimental peak values of bulk a-SiO_2 shows that these peaks occur at θ = 120°, 144°, and approximately 180°, the last value suggesting regions with possibly linear Si-O-Si bonds or large sized (8,9 and higher) rings. Comparison with the observed peaks in the interfacial region shows that the most dominant values of θ lie near 133° and 151° which may largely arise from 5 and 7 membered rings. In addition, in the interfacial region, peaks are observed at 101.60 eV, 100.4 eV, and 99.3 eV, which have been tentatively identified[2] as peaks due to Si^{+3}, Si^{+2}, and Si^{+1} states arising from Si_2O_3, SiO, and Si_2O structures. It is worthy of note that the chemical shifts of all these peaks scale identically with the binding energy shifts per unit charge calculated for bulk a-SiO_2 and SiO_2 in the interfacial region, the corresponding theoretically calculated peaks lying at 101.45 eV, 100.4 eV, and 99.35 eV.

We are presently investigating various aspects of the interplay between theory and experiment. The important message, nevertheless, is the conceptual framework presented here for the first time, within which interpretations of the valence and core levels of bulk and interfacial regions promises to be a fruitful avenue of investigation.

TABLE 1 Tight Binding Parameters Corresponding to Figs. 3 and 4 (Notation is as Shown in Fig. 1).

Matrix Elements	$E(sp^3)$	$E(P_{ox})$	V_1	$V_{sp\sigma}$	$V_{p\sigma\sigma}$	$V_{p\sigma\pi}$	$V_{p\pi\sigma}$	$V_{sp\pi}$	$V_{p\pi\pi}$	V_2	V_p
Set 1	12.40	-1.45	-1.6	-7.0	9.00	4.00	4.00	-0.8	-0.7	1.5	1.76
Set 2	12.59	-1.26	-1.1	-4.0	4.35	4.00	4.00	-0.8	-0.7	1.5	1.45

TABLE 2 Observed and Calculated Si(2p) Levels in Bulk a-SiO_2 and the Interfacial Region of Si/SiO_2 Interface. θ Denotes the Si-O-Si Bond Angle Corresponding to the Calculated Si(2p) Core Level Position.

BULK			INTERFACE		
Observed E_B [Si(2p)]	Calculated E_B [Si(2p)]	θ	Observed E_B [Si(2p)]	Calculated E_B [Si(2p)]	θ
103.0 eV	103.0 eV	~180°	102.7 eV	102.7 eV	150°
102.5 eV	102.5 eV	144°	102.3 eV	102.3 eV	135
102.1 eV	102.1 eV	120°			

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